Summary of Doctoral Dissertation (Doctoral Program (Science))※1

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Title: Design of (Arylimido)vanadium(V)-Alkylidene Complex Catalysts for Ring-Opening Metathesis Polymerization of Cyclic Olefins

※2 (Japanese): 環状オレフィンの開環メタセシス重合に有効な芳香族イミド配位バナジウム錯体触媒の創製（英文）

Summary

Olefin metathesis is one of a powerful method for C-C bond formation, which has broadened the synthetic routes for organic compounds, polymers, and advanced materials; design of the highly active catalysts has thus been of great interest. Metal-carbene (alkylidene) complexes are known to play a key role in this catalysis; Ru-carbene and Mo-, W-alkylidene catalysts are the well-known examples. Recently, study on synthesis and reaction chemistry of vanadium-alkylidene complexes has also been considered as an attractive subject,[1] however, the metathesis chemistry and the related organometallic chemistry have not been well understood due to the limited examples.[1,2] Synthesis of a series of (imido)vanadium(V)-alkylidene complexes containing anionic donor ligands,[1,2,3a] which catalyze ring-opening metathesis polymerization (ROMP) of norbornene (NBE) derivative have also been known, and the ligands affect the activities, especially the complex containing electron-withdrawing ligands, exemplified as $V(CHSiMe_3)(N\text{-}2,6\text{-}Cl_2C_6H_3)(OC_6F_5)(PMe_3)_2$ (**1**),[2,3a,b] exhibited the significant activities.

Since the ROMP by early transition metal complex catalysts have been limited to the high-strain monomers (e.g., NBE and its derivatives), in this thesis, a possibility of ROMP of low-strain cyclic olefins using phenoxy-modified (imido)vanadium(V)-alkylidene complex catalysts,[3c,d] and synthesis of the new copolymers[3b] including development of the stereospecific (*cis*-specific) catalysts have been explored in detail.

1. Synthesis of New Vanadium Alkylidene Complex Catalysts for Ring Opening Metathesis Polymerization (ROMP) of Low-Strain Cyclic Olefins.

A series of (arylimido)vanadium(V)-alkylidene complexes containing pentachloro-phenoxy ligands of the type, $V(CHSiMe_3)(N\text{-}2,6\text{-}R_2C_6H_3)(OC_6Cl_5)(PMe_3)_2$ [R = H (**2**), Cl (**3**), F (**4**), CH_3 (**5**)], were prepared from the reaction of trialkyl corresponding complexes, $V(N\text{-}2,6\text{-}R_2C_6H_3)(CH_2SiMe_3)_3$, with C_6Cl_5OH and subsequent addition of PMe_3. The isolated alkylidene complexes (**2**-**5**) were identified by NMR spectra and elemental analysis; the structure of complex **5** was also determined by x-ray crystallography. Two resonances ascribed to the alkylidene protons ascribed to *syn*/*anti*

forms were observed in the ^{1}H NMR spectra and in the ^{51}V NMR spectra.

A driving force in ROMP of cyclic olefins has been postulated a release of ring strain; NBE, high-strain monomer,[4a] has thus been chosen as a benchmark monomer to evaluate the catalytic activity. The activity in the ROMP of NBE by **1**-**5** (in benzene at 25 ºC) increased in the order: **5** < **2** << **4**, **3** < **1**, suggesting that an electronic factor in the imido ligand play a role; the OC_6F_5 analogue (**1**) showed the rather higher activity than the OC_6Cl_5 analogue (**3**). It turned out that ROMPs of low strain monomers [cyclopentene (CPE), cycloheptene (CHPE), and *cis*-cyclooctene (COE)] using the OC_6Cl_5 analogue, $V(CHSiMe_3)(N\text{-}2,6\text{-}Cl_2C_6H_3)(OC_6Cl_5)(PMe_3)_2$ (**3**) showed higher activity than the OC_6F_5 analogue (**1**), and the activities using the difluorophenylimido analogue (**4**) and by **3** increased in the order: COE << CHPE < CPE. Differences in the ring strain energies are not so significant (6.8, 6.7, and 7.4 kcal/mol for CPE, CHPE, and COE, respectively),[4a] suggesting that a release of ring strain is not the crucial factor in this vanadium catalysis. Moreover, complex (**3**) showed higher activity than the OC_6F_5 analogue (**1**), and the activity increased at high temperature; the activity increased even at 120 ºC upon addition of PMe_3.[3c] Similar trend was also observed by **1**.[3a,b] The polymer yields (TON) and the M_n values increased over time course without significant changes in the M_w/M_n values, and a linear relationship between the M_n values and polymer yields was clearly observed till high COE conversion (*ca.* 50 %). The high temperature ROMP by **3** at 80 ºC without catalyst decomposition or chain transfer reaction has thus been demonstrated.

2. Synthesis of New Copolymers *via* ROMP.

In order to demonstrate a promising potential in the vanadium catalysis, copolymerization via ROMP by using the vanadium alkylidene complex was examined. Since the activity in ROMP of COE was much lower than that in ROMP of NBE, due to this difference in the observed activities, the possibilities for synthesis of copolymers consisting of high-strain monomers [NBE or tetra-cyclododecene (TCD)] in the presence of low-strain monomer, COE, were explored.[3b] The resultant copolymers prepared by **1** possessed high molecular weights with unimodal molecular weight distributions. The resultant copolymers possess microstructure of repeated ring-opened TCD (or NBE) and certain methylene units by incorporation of ring-opened COE. On the basis of NMR spectra and DSC thermograms; hydrogenated poly(TCD-*bl*-COE) possessed melting temperature at 294 ºC.

3. Synthesis of New Catalyst for the Efficient *Cis*-specific ROMP.

Although ROMPs of low-strain monomers (CPE, CHPE and COE) could be achieved by **1** and **3**, the resultant polymers possess a mixture of *cis*/*trans* olefinic double bonds. *Cis* specific ROMP of NBE by catalyst containing fluorinated alkoxy ligands, $V(CHSiMe_3)(N\text{-}2,6\text{-}Cl_2C_6H_3)(OC(CF_3)_3)(PMe_3)_2$ (**6**), has been previously reported,[2b] but **6** showed negligible activities for ROMP of CHPE, COE. The pentafluorophenylimido analogue (**7**), newly prepared from $V(NC_6F_5)(CH_2SiMe_3)_3$,[5] exhibited higher activity

than **6** for ROMP of NBE, and the resultant ring-opened poly(NBE)s possessed highly *cis* olefinic double bonds (98 %). The complex **7** showed the activities for ROMP of CHPE at 25 °C, whereas **6** showed the negligible activity under the same conditions; the activity increased upon addition of $B(C_6F_5)_3$. The resultant poly(CHPE) prepared by **7** possessed highly *cis* olefinic double bonds (>99 %), clearly demonstrating that **7** enables *cis* specific ROMP of low-strain cyclic olefins for the first time.

Conclusion

A series of (arylimido)vanadium(V)-alkylidene complexes containing pentachlorophenoxy ligand of type, $V(CHSiMe_3)(N\text{-}2,6\text{-}R_2C_6H_3)(OC_6Cl_5)(PMe_3)_2$ [R = H (**2**), Cl (**3**), F (**4**), CH_3 (**5**)], has been prepared and identified; these complex catalysts exhibited from moderate to high catalytic activities for ROMP of cyclic olefins. It has been demonstrated that **3** showed higher efficiency for ROMP of low-strain monomers (CPE, CHPE, COE), which were difficult by ordinary early transition metals alkylidene catalysts. In particular, the ROMPs of CHPE and COE by **3** proceeded in a living manner and the livingness maintained even at 80 °C in the ROMP of COE. The ROMP of NBE, TCD in the presence of COE afforded multi-block copolymers consisting of repeated ring-opened TCD (or NBE) and certain methylene units by incorporation of COE on the basis of microstructural analysis by NMR spectra and the DSC thermograms. The *cis*-specific ROMP of low-strain monomer (CHPE) has been demonstrated for the first time by $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (**7**).

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